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Use of benzaldydes for the marking of hydrocarbons

Use of benzaldehydes of the formula,

[Please see original text]

in which
the ring A can be benzoanellated and
R^1, R^2 and R^3 signify hydrogen, hydroxy, C_1-C_{15}-alkyl, C_1-C_{15}-alkoxy, cyano, nitro or a group of the formula NR^4R^5 or $COOR^6$, in which
R^4 stands for hydrogen or optionally substituted C_1-C_{15} alkyl,
R^5 stands for optionally substituted C_1-C_{15} alkyl or a group of the formula L-NX^1-X^2, in which L possesses the signification of C_2-C_8 alkylene and X^1 and X^2 possess independently of one another the signification of C_1-C_6-alkyl or together with the nitrogen atom connecting them the signification of a heterocyclic group, and
R^6 stands for hydrogen, optionally substituted C_1-C_{15}-alkyl or for a group of the formula L-NX^1-X^2, in which L, X^1 and X^2 possess the above-mentioned signification respectively,
as a marking means for hydrocarbons, a method of detecting said benzaldehydes in hydrocarbons, and hydrocarbons containing the above-mentioned benzaldehydes.

The following details have been taken from the papers filed by the applicant

Description

The present invention relates to the use of benzaldehydes of Formula I

[Please see original text] (I)

in which

the ring A can be benzoanellated,

R^1, R^2 and R^3 signify independently of one another hydrogen, hydroxy, C_1–C_{15}-alkyl, C_1–C_{15}-alkoxy, cyano, nitro or a group of the formula NR^4R^5 or $COOR^6$, in which

R^4 stands for hydrogen or C_1–C_{15} alkyl, which can be interrupted by 1 to 4 oxygen atoms in ether function and optionally is substituted by phenyl,

R^5 stands for C_1–C_{15} alkyl, which can be interrupted by 1 to 4 oxygen atoms in ether function and optionally is substituted by phenyl, or a group of the formula L-NX^1-X^2, in which L possesses the signification of C_2–C_8 alkylene and X^1 and X^2 possess independently of one another the signification of C_1–C_6-alkyl or together with the nitrogen atom connecting them the signification of a 5- or 6-membered saturated heterocyclic group, which can contain an additional oxygen atom in the ring, and

R^6 stands for hydrogen, C_1–C_{15}-alkyl, which can be interrupted by 1 to 4 oxygen atoms in ether function, or for a group of the formula L-NX^1-X^2, in which L, X^1 and X^2 possess the above-mentioned signification respectively,

as a marking means for hydrocarbons, a method of detecting said benzaldehydes in hydrocarbons, and hydrocarbons containing the above-mentioned benzaldehydes.

There are already known from US-A-5 145 573, US-A-5 182 372 and from EP-A-499 845 azo dyes which serve as marking means for mineral oils. US-A-4 009 845 further discloses a method of marking mineral oils by means of disazo dyes, in which the dye added to the mineral oil is rendered visible by adding to the marked mineral oil an adsorbent which binds other coloured constituents of the mineral oil.

In DE-A-36 08 215 and DE-A-37 24 757 are disclosed benzopyran derivatives and their use in recording systems.

In Example 1 of DE-A-36 08 215 is disclosed the reacting of 2,3-dimethylbenzopyrylium-trichlorozincate with 4-dimethylaminobenzaldehyde in methanol with formation of the dye salt with the formula

[Please see original text]

In WO-A-11 466/1994 is disclosed the use of substituted anilines for the marking of mineral oils.

The object of the present invention was to provide novel means for the marking of hydrocarbons. The novel means were to be easily accessible and highly soluble in hydrocarbons. In addition, they were to be capable of being detected in a simple manner. In addition even very small amounts of marking substance were to be capable of being rendered visible by a strong colour reaction.

Accordingly it was found that the benzaldehydes of Formula I described in detail in the preamble are suitable with advantage as marking means for hydrocarbons.

All the alkyl and alkenyl groups contained in the above-mentioned Formula I can be both straight-chain and branched..

If X^1 and X^2 signify together with the nitrogen atom connecting them a 5- or 6-membered saturated heterocyclic group, which can contain an additional oxygen atom in the ring, pyrrolidinyl, piperidinyl or morpholinyl, for example, can be considered for the latter.

Groups R^1, R^2, R^3, R^4, R^5, R^6, X^1 and X^2 are e.g. methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, pentyl, isopentyl, neopentyl, tert-pentyl, hexyl or 2-methylpentyl.

Groups R^1, R^2, R^3, R^4, R^5 and R^6 are in addition e.g. heptyl, octyl, 2-ethylhexyl, isooctyl, nonyl, isononyl, decyl, isodecyl, undecyl, dodecyl, tridecyl, 3,5,5,7-tetramethylnonyl, isotridecyl, tetradecyl or pentadecyl (the above names isooctyl, isononyl, isodecyl and isotridecyl are trivial names and come from the alcohols obtained by oxosynthesis – cf. for this Ullmann's Encyclopedia of Industrial Chemistry, 5th Edition, Vol. A1, pp. 290 to 293, and Vol. A 10, pp. 284 and 285).

Groups R^1, R^2 and R^3 are in addition e.g. methoxy, ethoxy, propoxy, isopropoxy, butoxy, isobutoxy, sec-butoxy, pentyloxy, isopentyloxy, neopentyloxy, tert-pentyloxy, hexyloxy, 2-methylpentyloxy, heptyloxy, octyloxy, 2-ethylhexyloxy, isoocytyloxy, nonyloxy, isononyloxy, decyloxy, isodecyloxy, undecyloxy, dodecyloxy, tridecyloxy, 3,5,5,7-tetramethylnonyloxy, isotridecyloxy, tetradecyloxy or pentadecyloxy.

Groups R^4 and R^5 are in addition e.g. 2-methoxyethyl, 2-ethoxyethyl, 2-propoxyethyl, 2-isopropoxyethyl, 2-butoxyethyl, 2- or 3-methoxypropyl, 2- or 3-ethoxypropyl, 2- or 3-propoxypropyl, 2- or 3- butoxypropyl, 2- or 4-methoxybutyl, 2- or 4- ethoxybutyl, 2- or 4-propoxybutyl, 2- or 4-butoxybutyl, 3,6-dioxaheptyl, 3,6-dioxaoctyl, 4,8-dioxanonyl, 3,7-dioxaoctyl, 3,7-dioxanonyl, 4,7-dioxaoctyl, 4,7-dioxanonyl, 4,8-dioxadecyl, 3,6,8-trioxadecyl, 3,6,9-trioxaundecyl, 3,6,9,12-tetraoxatridecyl, benzyl or 1- or 2-phenylethyl.

Groups L are e.g. $(CH_2)_2$, $(CH_2)_3$, $(CH_2)_4$, $(CH_2)_5$, $(CH_2)_6$, $(CH_2)_7$, $(CH_2)_8$, $CH(CH_3)CH_2$ or $CH(CH_3)CH(CH_3)$.

Preferably used according to the invention are benzaldehydes of Formula I in which at least one of the groups R^1 to R^3 signifies a group with the formula NR^4R^5, in which R^4 and R^5 each possess the above-mentioned signification respectively.

Particularly preferably benzaldehydes of Formula Ia

[Please see original text] (Ia),

in which R^1, R^2, R^4 and R^5 possesses the above-mentioned signification respectively, are used for the marking of hydrocarbons.

Particularly suitable are benzaldehydes of Formula Ia, in which R^1 and R^2 signify independently of one another respectively hydrogen, hydroxy, C_1–C_{15} alkyl, C_1–C_{15} alkoxy or a group with the formula $COOR^6$, in which R^6 possesses the above-mentioned signification, R^4 signifies hydrogen or C_1–C_{15} alkyl and R^5 signifies C_1–C_{15} alkyl.

Particularly preferred are benzaldehydes of Formula Ia, in which R^4 and R^5 signify independently of one another respectively C_1 –C_{13} alkyl, and R^1 and R^2 respectively hydrogen, for the marking of hydrocarbons.

The subject of the invention is furthermore a method of detecting the presence of benzaldehydes of Formula I in hydrocarbons, in which the hydrocarbon is treated with an aqueous-alcoholic or alcoholic medium which contains a proton acid, at least one compound of the group of compounds consisting of substituted benzopyrilium salts of Formula II

[Please see original text] (II),

in which R^7 stands for C_1–C_8 alkyl, phenyl, C_1–C_5 alkoxy or halogen and R^8 stands for methyl and R^7 and R^8 stand together for 1,4-butylene and the ring B can be annellated by a benzene ring and optionally is substituted by C_1–C_4 alkyl, pyrrolidino, piperidino, morpholino, chlorine or bromine or in ring position 7 optionally also by hydroxy, C_1–C_4 alkoxy, C_1–C_5 mono- or dialkylamino, which can be substituted respectively in turn by chlorine or phenyl, and X^e signifies any anion, and indoles of Formula III

[Please see original text] (III),

in which R^9 and R^{10} stand independently of one another for hydrogen, hydroxy, a group of the formula NR^4R^5, in which R^4 and R^5 possess respectively the above-mentioned signification, C_1–C_8 alkyl, phenyl, C_1–C_5 alkoxy or halogen,
and optionally a halide of the metals zinc, aluminium or tin.

Preferably used according to the invention are indoles of Formula III, in particular 2-phenylindole.

Examples of suitable anions X^7 are tetrachlorozincate, halide, sulfate, tetrafluoroborate or phosphate.

The benzaldehydes I, the benzopyrilium salts II and the indoles III are as a rule known per se.

By marking in the sense according to the invention is to be understood an addition of the benzaldehydes of Formula I to hydrocarbons in a concentration such that the hydrocarbons are thereby coloured in a manner either completely invisible or only slightly visible to the human eye, wherein however the benzaldehydes of Formula I are detectable easily and fully visibly by the detection methods described in detail here.

A further subject of the present invention is hydrocarbons containing one or more benzaldehydes of Formula I.

By hydrocarbons in the sense according to the invention are to be understood aliphatic or aromatic hydrocarbons which are present in a liquid state of aggregation under normal conditions.

These are in particular mineral oils, for example fuel oils such as benzene, kerosene or diesel oil, or oils such as heating oil or engine oil.

The benzaldehydes of Formula I are suitable in particular for the marking of mineral oils for which a labelling is required, e.g. on fiscal grounds. In order to keep the costs of the labelling low, attempts are made here to use the smallest possible amounts of marking means for the marking.

For the marking of hydrocarbons, the benzadehydes of Formula I are used either as a substance or in the form of solutions. Organic solvents are suitable as solvents. Preferably aromatic hydrocarbons such as toluene, xylene, dodecylbenzene, diisopropyl napththalene or a mixture of higher aromatics which is marketed under the name Shellsol® AB (firm Shell) are used. In order to avoid a high viscosity of the resulting solutions, a concentration of benzaldehydes I of 5 to 80 wt %, referred to the solution, is generally chosen.

To improve the solubility, still further co-solvents, e.g. alcohols such as methanol, ethanol, propanol, isopropanol, butanol, isobutanol, pentanol, hexanol, heptanol, octanol, 2-ethylhexanol or cyclohexanol, glycols such as butylethylene glycol or methylpropylene glycol, amines such as triethylamine, diisooctylamine, dicyclohexylamine, aniline, N-methylaniline, N,N-dimethylaniline, toluidine or xylidine, alkanolamines such as 3-(2-methoxyethoxy)propylamine, o-cresol, m-cresol or p-cresol, ketones such as diethyl ketone or cyclohexanone, lactams such as γ-butyrolactone, carbonates such as ethyl carbonate or propylene carbonate, phenols such as t-butylphenol or nonylphenol, esters such as methyl phthalate, ethyl phthalate, (2-

ethylhexyl)phthalate, ethyl acetate, butyl acetate or cyclohexyl acetate, amides such as N,N-dimethyl formamide, N,N-diethyl acetamide or N-methyl pyrrolidone, or their mixtures can also be used.

The use of the benzaldehydes of Formula I to be used according to the invention makes it very simple to detect marked hydrocarbons even if the marking substances are present in a concentration of only about 10 ppm or less.

The detection of the presence in hydrocarbons of the compounds of Formula I used as marking materials can be performed with advantage if the hydrocarbon is treated with an aqueous-alcoholic or alcoholic medium which contains a pyrilium salt of Formula II and/or an indole of Formula III, a proton acid and optionally a halide of the metals zinc, aluminium or tin. If aqueous-alcoholic media are used, the ratio by weight water : alcohol comes to 0.5 : 1 to 4 : 1, preferably approx. 1 : 1. A clearly visible colour change of the aqueous-alcoholic phase is obtained.

Suitable alcohols are e.g. ethanol, propanol, isopropanol, 1-methoxypropan-2-ol, ethylene glycol or 1,2- or 1,3-propylene glycol. The use of ethanol is preferred.

Suitable proton acids for the methods according to the invention are in particular so-called strong acids, i.e. proton acids whose pKa value is ≤ 3.5. There can be considered as such acids, for example, inorganic or organic acids such as perchloric acid, hydroiodic acid, hydrochloric acid, hydrobromic acid, hydrofluoric acid, sulfuric acid, nitric acid, phosphoric acid, benzenesulfonic acid, toluenesulfonic acid, napththalenesulfonic acid, methanesulfonic acid, oxalic acid, maleic acid, chloroacetic acid, dichloroacetic acid or bromoacetic acid. In some cases it may be advantageous to buffer said acids e.g. by the addition of acetic acid.
Apart from o- or p-toluenesulfonic acid, inorganic acids in particular are to be emphasised, wherein hydrochloric acid or sulfuric acid merit particular attention.

Suitable halides of the metals zinc, aluminium or tin are e.g. zinc chloride, zinc bromide, aluminium chloride, aluminium bromide or tin(IV) chloride. Zinc chloride is to be particularly emphasised.

It suffices as a rule to shake out an amount of about 10 to 50 ml of the hydrocarbon marked according to the invention with 1 to 50 ml of an aqueous-alcoholic or alcoholic solution of a pyrilium salt of Formula II and/or an indole of Formula III, a proton acid, optionally with the addition of the metal halide, in order to obtain a colour change. It is also possible to use, instead of the solution of the proton acid, an aqueous-alcoholic solution of the metal halide on its own, since the latter also has an acid reaction.

The concentration of the proton acid in the aqueous-alcoholic or alcoholic solution comes as a rule to 5 to 50 wt %, preferably 10 to 30 wt %. The concentration of metal halide is in general from 0 to 50 wt %, preferably from 5 to 20%, referred in each case to the weight of the solution.

A great advantage of the invention consists in the fact that two different methods of detecting the benzaldehydes of Formula I can be used. The detection can therefore also be carried out very reliably where there are possible disturbing influences (e.g. additives in diesel fuel).

The following examples serve to explain the invention in detail.

General procedure 1

Commercial diesel fuel was mixed in each case with 10 ppm of a benzaldehyde. For this 0.1 wt % of the aldehyde was pre-dissolved in toluene and said mixture was added to the diesel fuel.

In the following examples 1 to 12, 10 ml of diesel fuel so marked was mixed in each case with 2 ml of reagent solution and shaken for 5 minutes. 1 ml of water was then added and the product was shaken for a further 5 minutes. The aqueous phase showed the colours given in the following Table no. 1.

Reagent solution 1:

5 ml 1-wt-% indole in ethanol
5 ml hydrochloric acid conc.
5 g zinc chloride
95 ml acetic acid

Reagent solution 2:

5 ml 1-wt-% 2-methylindole in ethanol
5 ml hydrochloric acid conc.
5 g zinc chloride
95 ml acetic acid

Reagent solution 3:

5 ml 1-wt-% 2-phenylindole in ethanol
5 ml hydrochloric acid conc.
5 g zinc chloride
95 ml acetic acid

Particularly advantageous results are obtained if the diesel fuel is first of all filtered through silica gel.

Table 1

[Please see original text for Aldehyde formulae]

Ex no.	Aldehyde	Reagent	Colour
1		1	colour
2		2	violet
3		3	violet
4		1	orange
5		2	red-violet
6		3	magenta
7		1	orange
8		2	red-violet
9		3	magenta
10		1	red-violet
11		2	blue-violet
12		3	blue-violet

Similarly favourable results are obtained if the benzaldehydes listed in the following Table no. 2 are used as marking means:

Table no. 2
[Please see original text for Aldehyde formulae]

Ex. no.	Aldehyde
13	
14	
15	
16	
17	
18	
19	
20	

General procedure 2

Commercial diesel fuel was mixed in each case with 10 ppm of benzaldehyde. For this 0.1 wt % of the benzaldehyde was pre-dissolved in toluene and said mixture was added to the diesel fuel.

In Examples 21 to 30, 10 ml of the marked diesel fuel was mixed in each case with 2 ml of reagent solution 4 and refluxed for 5 minutes. 1 ml of water/ethanol (1 : 1 v/v) was then added and the product shaken for a further 5 minutes. The aqueous phase showed the colour given in the following Table no. 3.

Reagent solution 4

5 ml of benzopyrilium salt of the formula:

[Please see original text]

1-wt-% in water

25 ml hydrochloric acid conc.

225 ml acetic acid

Table 3

[Please see original text for Aldehyde formulae]

Ex. no.	Aldehyde	Q	Colour
21		C_6H_5	blue
22		CH_3	blue
23		C_6H_5	blue
24		H	blue
25		CH_3	blue
26		CH_3	blue
27		H	blue
28		CH_3	red-violet
29		CH_3	red-violet
30		CH_3	violet

Similarly favourable results are obtained if the benzopyrilium salt contained in reagent solution 5 is replaced by that with the formula

[Please see original text]

<u>Claims</u>

1. Use of benzaldehydes of Formula I

[Please see original text for Aldehyde formulae] (I)

in which
the ring A can be benzoanellated and
R^1, R^2 and R^3 signify independently of one another hydrogen, hydroxy, C_1-C_{15}-alkyl, C_1-C_{15}-alkoxy, cyano, nitro or a group of the formula NR^4R^5 or $COOR^6$, in which
R^4 stands for hydrogen or C_1-C_{15} alkyl, which can be interrupted by 1 to 4 oxygen atoms in ether function and is optionally substituted by phenyl,
R^5 stands for C_1-C_{15} alkyl, which can be interrupted by 1 to 4 oxygen atoms in ether function and is optionally substituted by phenyl, or a group of the formula L-NX^1-X^2, in which L possesses the signification of C_2-C_8 alkylene and X^1 and X^2 possess independently of one another the signification of C_1-C_6-alkyl or together with the nitrogen atom connecting them the signification of a 5- or 6-membered saturated heterocyclic group, which can contain an additional oxygen atom in the ring, and
R^6 stands for hydrogen, C_1-C_{15}-alkyl, which can be interrupted by 1 to 4 oxygen atoms in ether function, or for a group of the formula L-NX^1-X^2, in which L, X^1 and X^2 possess the above-mentioned signification respectively,
as marking means for hydrocarbons.

2. Use of benzaldehydes according to claim 1, characterised in that the benzaldydes correspond to Formula Ia

[Please see original text] (Ia)

in which R^1, R^2, R^4 and R^5 possess respectively the signification given in claim 1.

3. Use of benzaldehydes according to claims 1 or 2, characterised in that R^1 and R^2 signify independently of one another respectively hydrogen, hydroxy, C_1-C_{15}-alkyl, C_1-C_{15}-alkoxy or a group of the formula $COOR^6$, in which R^6 possesses the signification given in claim 1, R^4 signifies hydrogen or C_1-C_{15} alkyl and R^5 signifies C_1-C_{15} alkyl.

4. Method of detecting the presence of benzaldehydes of Formula I according to claim 1 in hydrocarbons, characterised in that the hydrocarbon is treated with an aqueous-alcoholic or alcoholic medium which contains a proton acid, at least one compound from the group of compounds consisting of substituted benzopyrilium salts of Formula II

[Please see original text] (II),

in which R^7 stands for C_1–C_8 alkyl, phenyl, C_1–C_5 alkoxy or halogen and R^8 stands for methyl and R^7 and R^8 stand together for 1,4-butylene and the ring B can be annellated by a benzene ring and optionally is substituted by C_1–C_4 alkyl, pyrrolidino, piperidino, morpholino, chlorine or bromine or in ring position 7 optionally also by hydroxy, C_1–C_4 alkoxy, C_1–C_5 mono- or dialkylamino, which can each by substituted in turn by chlorine or phenyl, and $X^?$ signifies any anion, and indoles of Formula III

[Please see original text] (III),

in which R^9 and R^{10} stand independently of one another respectively for hydrogen, hydroxy, a group of the formula NR^4R^5, in which R^4 and R^5 possess respectively the signification given in claim 1, C_1–C_8 alkyl, phenyl, C_1–C_5 alkoxy or halogen,
and optionally a halide of the metals zinc, aluminium or tin.

5. Hydrocarbons containing as marking means one or more benzaldehydes of Formula I according to claim 1.

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